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Molecular hyperpolarizabilities

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We report a systematic study of the first and second hyperpolarizabilities of several small molecules at a consistent level of theory and basis sets. Coupled cluster (CC) methods for correlation, analytical high-order time dependent Hartree-Fock (TDHF) theory for dispersion effects, and polarizability-consistent basis sets give agreement to about 10% between the calculated hyperpolarizabilities and the gas phase experiments for the nonpolar molecules, H_2 , N_2 , CO_2 , and C_2H_4 , and effectively nonpolar CO. Results for the polar molecules FH, H_2O , NH_3 , and H_2S are improved by adding lone-pair basis functions. For H_2O and NH_3 there is good ($\sim 10\%$) agreement with experiment. However, a $\sim 20\%$ difference between experiment and theory for the FH molecule persists; this difference is discussed in some detail.

INTRODUCTION

Primarily because of their role in the nonlinear optical properties of molecules, hyperpolarizabilities have recently received much attention.¹⁻³ Hyperpolarizabilities are defined as the coefficients in the series expansion of the energy (or dipole) in the presence of an oscillating electric field. In the static case this expansion becomes $E(F) = E_0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - (1/3!) \beta_{ijk} F_i F_j F_k - (1/4!) \gamma_{ijkl} F_i F_j F_k F_l + \dots$ (Einstein summation convention assumed), with β_{ijk} and γ_{ijkl} being the components of the first and second hyperpolarizability tensor. In addition to potential applications to optical material design, which requires a knowledge of the β and γ tensors, there are also a number of other unsolved questions. Some of these concern inconsistencies in the experimental values which cannot be explained by the different dispersion effects encountered in the various experimental procedures. However, there are also significant inconsistencies between theory and experiment, and between theory and theory. An understanding of molecular nonlinear optical behavior requires resolving these existing differences. The objective of this paper is to present a systematic study of theoretical calculations for several small molecules whose gas phase experimental values are well known.^{4,5} This, combined with comparisons with other calculations, provides some calibration of the accuracy of high-level quantum chemical methods.

The reliable *ab initio* prediction of molecular hyperpolarizabilities requires several elements: basis sets, electron correlation, frequency dependent (dispersion) effects, and vibrational corrections. First, basis sets have to be adequate. The prediction of hyperpolarizabilities depends upon products of matrix elements of the electron position operator, \hat{r} . Consequently, unlike the molecule's energy, which primarily depends upon inverse powers of \hat{r} , any study of hyperpolarizabilities must allow for an adequate description of the more diffuse regions of the molecule's wave function. Basis sets that are usually found to be adequate for a dipole moment require further extension to adequately account for the polarizability tensor, α , and even further extensions for the first hyperpolarizability, β ,

or for the second hyperpolarizability, γ . There are also other factors. Namely, all contributions to α have the same sign, so the larger the basis generally the better, and this is usually true of γ as well; but the relative values of the charge density must also be described in β (or μ) and that imposes additional restrictions on a balanced description. To emphasize the basis set aspect, the SCF values for static $\gamma_{||} = (\gamma_{iijj} + \gamma_{ijji} + \gamma_{jiji})/15$ (summation convention) for ethylene are -37 a.u. at the STO-3G level, -241 for a DZ basis; 6230 for a 6-31G+diffuse (*s,p*) basis, and 6440 with a (5s3p2d/3s2p1d) basis. Of course, the SCF result reflects just a part of a basis set's effect, as the introduction of electron correlation requires a much larger and more flexible Hilbert space.

After basis sets, the accurate inclusion of electron correlation is the next most important factor in attaining reliable values.⁶⁻¹⁹ The initial studies of correlated molecular hyperpolarizabilities^{6,7} already demonstrated that for the small, polar molecules FH and H_2O , correlation could change the predicted β static hyperpolarizabilities by as much as a factor of 2 and have a large effect on γ . This fact has now been supported by several other correlated studies,⁸⁻¹⁸ and also applies to recent results for larger molecules like para-nitroaniline.¹⁹ For nonpolar molecules like N_2 ,^{10,16} *trans*-butadiene,^{16,17} benzene,¹² and the nearly nonpolar CO,¹⁷ there are similarly significant (40%–60%) increases in $\gamma_{||}$ due to effects of electron correlation. Powerful, coupled-cluster (CC)²⁰ and many-body perturbation theory (MBPT)²¹ methods are used here for the treatment of electron correlation for static hyperpolarizabilities.

Since hyperpolarizabilities require third and fourth derivatives of the energy with respect to a field, a purely finite-field approach requires several energy calculations to determine all tensor components and can sometimes suffer from numerical imprecision. By virtue of computing the induced dipole moment in the presence of a field analytically, via recently developed analytical first derivative methods that introduce a "relaxed density,"²² which is now implemented for the CCSD method and various orders of MBPT²³ including those that include triple excitations, MBPT(4),²⁴ CCSD + T(CCSD), CCSD(T), and

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QCISD(T),²⁵ the numerical precision can be improved by a couple of orders of magnitude.

The third important factor is the frequency dependence of the hyperpolarizability. First, without the inclusion of the frequency dependence, the various experimentally distinct nonlinear processes that occur would coincide in the static limit. For β , i.e., second harmonic generation (SHG); optical rectification (OR); and the electro optic Pockels effect (EOPE); and for γ , i.e., third harmonic generation (THG), dc induced second harmonic generation (dc-SHG), intensity dependent refractive index (IDRI), electro-optical Kerr effect (EOKE), and dc induced optical rectification (dc-OR). Second, dispersion effects can have a relatively large effect on the observed hyperpolarizability, and predictive calculations will frequently require more accurate dispersion values than those estimated. This would be particularly true if the exciting frequency (ω) becomes close to a resonance, and for SHG a resonance will occur at $\omega/2$ and for THG $\omega/3$, further compounding the problem. A knowledge of the frequency dependence is also important in identifying possible resonance enhanced effects that might suit a particular molecule to a specific application.

In order to describe the frequency dependent effects, we have developed an open-ended, analytical, high-order time dependent Hartree-Fock (TDHF) approach²⁶ for hyperpolarizabilities. This permits the analytical evaluation of any order hyperpolarizability tensor. In the static ($\omega=0$) limit this reduces to Dykstra's open-ended derivative Hartree-Fock (DHF) method.²⁷ Others have now written similar TDHF programs which employ the $2n+1$ rule for β ²⁸ and for β and γ ,²⁹ while our original procedure permits the higher polarizabilities δ, ϵ, \dots , to be readily obtained as well. Because of the absence of electron correlation, the TDHF theory is not usually sufficient, alone, to predict the absolute value of such properties. Others have considered the more general formulation of frequency dependent hyperpolarizabilities.^{18,30,31} However, we observe that correlated static values augmented by the *percentage correction* for the frequency dependence given by TDHF¹⁶ seems generally justified. In cases where the correlated frequency dependence is known from MBPT(2),¹⁸ or from multiconfiguration linear response (MCLR) calculations,³¹ the TDHF percentage dispersion is quite close. Recently, we reformulated our original atomic-orbital-basis higher-order TDHF computational algorithm in the molecular orbital basis to exploit simplifications in the Fock matrices that permit a more efficient application of TDHF theory for many molecular systems.¹⁷ The program also exploits the $2n$ rule for calculating the hyperpolarizabilities.

Vibrational corrections are also sometimes important in obtaining predictive accuracy for molecular hyperpolarizabilities. There are two types: the first simply involves averaging over the zero-point vibration; while the second, β_{vib} and γ_{vib} , involves contributions to the hyperpolarizability from vibronic intermediate states.^{2,3} Both have been previously considered in calculations^{7,8,12,34} and experimentally.³⁵

In the following, after a discussion of the computational methods, we present results for the molecules H_2 , N_2 , CO , CO_2 , C_2H_4 , FH , H_2O , NH_3 , and H_2S with augmented, polarizability consistent basis sets derived from Sadlej.³⁶

COMPUTATIONAL PROCEDURES

The following results obtained for static and frequency dependent hyperpolarizabilities are obtained with the ACES II program system.³⁷ See Ref. 16 for the relevant equations. SCF static results are augmented by correlated results at the MBPT(2), CCSD,³⁸ and CCSD(T)^{39,40} levels. At the SCF level all hyperpolarizabilities are obtained analytically from our TDHF program for $\omega=0$. At the correlated levels, depending upon symmetry for the field dependent calculations, we either evaluate the dipole moment in the presence of an electric field, analytically, from which subsequent numerical differentiation provides static α , β , and γ ; or take high-order energy derivatives. In ACES II,³⁷ we also can compute analytical second derivatives (i.e., α) at the MBPT(2) level,^{41,42} which permits β and γ to be obtained by subsequent numerical differentiation. Field strengths are chosen to be 0.005 a.u., which we have found acceptable in previous studies.⁸ The direct computation of derivatives is numerically preferable to a sum over states (SOS) method since no truncation of states need be made. The interpretative value of the two- and three-state models⁴³ that arises from the SOS procedure is lost, however.

We introduce frequency dependence for the various optical processes via TDHF calculations at the appropriate ω . We analytically compute all the different possible processes and components for β and γ , without using Kleinman symmetry.^{1(d)} The correlated results are scaled by the TDHF *percentage* dispersion. For cases where the correlated dispersion is known,^{18,31} we observe that for NH_3 the SHG-TDHF dispersion at 0.06 a.u. (close to the ruby laser frequency of 0.0656 a.u.) gives 35% which is exactly that for MBPT(2) and 17% compared to 23% for H_2CO . Similarly, for EOKE, TDHF gives 10% compared to 9.8% in second order for NH_3 , and 5.1% compared to 6.4% for H_2CO .¹⁸ For FH, the dispersion of the MCLR SHG results at $\omega=0.06$ a.u. also appears to be effectively parallel to those from TDHF.³¹ For γ less correlated dispersion information is available. For FH, MCLR calculations report 19% for dc-SHG compared to 15% obtained by TDHF.³¹ The other errors in the calculations reported are such that a few percent difference between TDHF and the correct dispersion will not change any conclusions regarding our results. Of course, TDHF and correlated frequency dependent methods will fail near a resonance so such situations are excluded. All results reported here are for the ruby laser frequency.

Except where noted, the molecular geometry is assumed to be at the experimental equilibrium, shown in Table I. In each case our initial basis is chosen to be the polarizability consistent basis (POL) set recommended by Sadlej.³⁶ To report results for a large number of examples, we choose this basis set because it has modest size yet

TABLE I. Molecular geometries and location of lone pair basis functions.^a

CO ₂	$D_{\infty h}$; $R_{CO}=1.612\ 26\ \text{\AA}=2.1944\ \text{a.u.}$
H ₂ O	C_{2v} ; $R_{HO}=0.957\ \text{\AA}$; $\angle \Theta_{HOH}=104.5^\circ$. Two lone pair basis sets are located in the plane perpendicular to the molecular plane with a distance of $0.883\ \text{\AA}$ from O and the angle between the lone pair being 118° .
HF	$C_{\infty v}$; $R_{HF}=0.917\ \text{\AA}=1.7328\ \text{a.u.}$; $R_{HF}^0=0.932=1.7621\ \text{a.u.}$ Three lone pair basis sets are located at the position of the bond distance R_{HF} with tetrahedral angles.
NH ₃	C_{3v} ; $R_{NH}=1.012\ \text{\AA}$; $\angle \Theta_{HNN}=106.7^\circ$. One lone pair basis set is located in the molecular axis with the bond distance R_{NH} .
CO	$C_{\infty v}$; $R_{CO}=1.128\ 32\ \text{\AA}=2.132\ 221\ \text{a.u.}$
N ₂	$D_{\infty h}$; $R_{NN}=1.097\ 68\ \text{\AA}=2.074\ 32\ \text{a.u.}$
H ₂	$D_{\infty h}$; $R_{HH}=0.740\ 847\ 97\ \text{\AA}=1.4\ \text{a.u.}$
H ₂ S	C_{2v} ; $R_{HS}=1.3280\ \text{\AA}$; $\angle \Theta_{HSH}=92.2^\circ$; two lone pair basis sets are located in the plane perpendicular to the molecular plane at a distance of $1.328\ \text{\AA}$ from S and the angle between the lone pairs being 92.2° .
C ₂ H ₄	D_{2h} ; $R_{CC}=1.34\ \text{\AA}$; $\angle \Theta_{HCC}=\angle \Theta_{HCH}=120^\circ$; $R_{HC}=1.08\ \text{\AA}$.

^aSpectroscopic Data Relative to Diatomic Molecules (Pergamon, New York, 1970); Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 18 (The Chemical Society, London, 1965).

almost the same quality as larger ANO basis sets⁴⁴ in its ability to reproduce the molecular dipole polarizabilities in correlated calculations.³⁶ We identify the POL basis as basis set 1. Basis set 2 is created from basis set 1 by augmenting the POL basis with a set of *d*-type Cartesian Gaussian functions ($\zeta_d=0.1$) for hydrogen. The exponent is chosen to reproduce the hydrogen molecule hyperpolarizability. Since the basis is intended to be used in larger molecular systems, only one set of extra functions is added. As will be seen, these extra polarization functions are very important in describing the high polarization of the hydrogen atom.

For the polar molecules FH, H₂O, NH₃, and H₂S, we use an unconventional type of basis as basis set 3. This basis adds to basis set 2 lone-pair functions which consist of an *s* and a set of *p* functions ($\zeta_{s,p}=0.1$) located in the lone-pair direction (see Table I) with the same distance from the heavy atom X, as X-H where X=N, O, F, or S. Our objectives in introducing lone-pair functions include the following:

- (1) To introduce a dramatic change compared to conventional atom centered basis sets to partly assess the degree of basis set convergence;
- (2) to alleviate the necessity of adding many high angular momentum polarization functions to the heavy atom;
- (3) to provide a description more specific to lone pairs, which are generally less well described in more conventional quantum chemical basis sets. Comparisons with extensive atom centered basis sets are considered in the Discussion.

RESULTS AND DISCUSSION

CO₂

For the nonpolar CO₂ molecule, results are shown in Table II. The first observation is that the SCF components

of the polarizability in the POL basis are quite similar to the large basis (5s4p3d1f) results of Amos *et al.*⁴⁵ who find $\alpha_{zz}=23.7$ and $\alpha_{xx}=11.9$. Other extensive basis (6s4p4d1f) results of Maroulis and Thakkar give 23.7 and 12.0.^{9(b)} Visser and Wormer in a (6s5p3d2f) basis obtain 23.6 and 11.9,⁴⁶ as well. Correlation has a significant effect of about 10% giving $\bar{\alpha}=17.6$ for CCSD(T), which agrees well with experiment and with the SDQ-MBPT(4) value.^{9(b)} SDQ(4) is the fourth-order approximation to CCSD, which offers the more appropriate comparison, however. As usual, the anisotropy is less accurate, but our CCSD(T) value of 14.5 (or CCSD of 14.4) compares quite well with the SDQ(4) result of 14.3.^{9(b)}

The static SCF second hyperpolarizability $\gamma_{||}$ is 800 a.u., which is about 60% of the dc-SHG experimental value of 1332 a.u.. MBPT(2) improves the result at the static limit to 1170 a.u., i.e., a $\sim 30\%$ improvement. The effect of infinite-order correlation as measured by CCSD actually reduces the correlation effect to give 1070 a.u. Introducing TDHF dispersion increases $\gamma_{||}$ by 31% (or accounts for 13% of the experimental value) for THG and 13% (or 8% of experiment) for dc-SHG. Scaling by the

TABLE II. Components of the polarizability and second hyperpolarizabilities of the CO₂ molecule and results for various processes (in a.u.).^a

	SCF/ TDHF ^b	MBPT(2) ^c	CCSD ^d	CCSD(T) ^e	EXP
$\alpha_{xx}=\alpha_{yy}$ ^a	11.8101	12.8638	12.6327	12.7908	
α_{zz}	23.8862	27.8482	27.0631	27.2984	
$\bar{\alpha}$ ^c	15.835	17.859	17.443	17.627	17.50 ^f
$\Delta\alpha$ ^d	12.076	14.984	14.430	14.508	13.83 ^f
γ_{xxxx}	700.0	1010.0	930.0	900.0	
γ_{zzzz}	810.0	1120.0	900.0	1030.0	
γ_{xxzz}	330.0	500.0	490.0	520.0	
$\gamma_{ }$ ^e	800.0	1170.0	1070.0	1150.0	
THG ^h	1046.0	1500.0	1400.0	1500.0	1860 \pm 270 ⁱ
dc-SHG ^j	910.0	1300.0	1200.0	1300.0	1332 \pm 15 ^m
IDRI ^k	871.0	1300.0	1200.0	1200.0	
EOKe ^k	833.0	1200.0	1100.0	1200.0	

^aThe *z* axis is the principal axis of the molecule.

^bIn this and subsequent tables, frequency dependent polarizabilities are evaluated at $\omega=0.0656\ \text{a.u.}=6443\ \text{\AA}$.

^c $\bar{\alpha}=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$.

^d $\Delta\alpha=\frac{1}{2}[(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{xx}-\alpha_{zz})^2+(\alpha_{yy}-\alpha_{zz})^2]^{1/2}$.

^e $\gamma_{||}=(\gamma_{xxxx}+\gamma_{yyzz}+\gamma_{zzzz})/15$ with Einstein summation convention.

^fM. A. Spackman, J. Phys. Chem. **93**, 7594 (1989), obtains these values from analysis of several different experiments.

^gCorrelated frequency dependent values are estimated by $\gamma_{||}^{\text{corr}}(\omega)=(\gamma_{||}^{\text{TDHF}}(\omega)/\gamma_{||}^{\text{SCF}}(0))\times\gamma_{||}^{\text{corr}}(0)$ in this and subsequent tables.

^hTHG: third harmonic generation, $\gamma(-3\omega;\omega,\omega,\omega)$.

ⁱdc-SHG: dc-induced second harmonic generation, $\gamma(-2\omega;\omega,\omega,0)$.

^jIDRI: intensity dependent refractive index, $\gamma(-\omega;\omega,\omega,-\omega)$.

^kEOKe: electro-optic Kerr effect, $\gamma(-\omega;\omega,0,0)$. dc-OR: dc-induced optical rectification, $\gamma(0;\omega,-\omega,0)$ is numerically the same as EOKe after averaging.

^lReference 5. Since $\chi^{(1)}_{||}=\gamma_{||}/6$ conversion factor is $\frac{1}{6}\times 5.03\times 10^{-43}\ \text{esu/molecule/a.u.}=8.395\times 10^{-41}\ \text{esu/molecule/a.u.}$

^mReference 4.

TABLE III. Components of the polarizability and second hyperpolarizabilities of the N_2 molecule and results for various processes (in a.u.)^a

	SCF/ TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
$\alpha_{xx} = \alpha_{yy}$	9.6310	9.9750	10.0002	10.1290	
α_{zz}	15.0033	14.4138	14.8266	14.9975	
$\bar{\alpha}$	11.422	11.455	11.609	11.752	11.8 ^b
$\Delta\alpha$	5.372	4.439	4.826	4.869	4.67 ^b
γ_{xxxx}	660.0	780.0	810.0	860.0	
γ_{zzzz}	790.0	1220.0	1220.0	1290.0	
γ_{xxzz}	270.0	340.0	350.0	370.0	
γ_{\parallel}	730.0	930.0	950.0	1010.0	
THG ^c	937.0	1200.0	1200.0	1300.0	1270.0 ^d
dc-SHG	822.0	1100.0	1100.0	1100.0	1030 \pm 12 ^d
IDRI	788.0	1000.0	1000.0	1100.0	
EKE	756.0	1000.0	1000.0	1100.0	

^aThe z axis is the principal axis of the molecule. γ_{\parallel} , $\bar{\alpha}$, $\Delta\alpha$ are defined in the footnotes of Table II.

^bA. D. Buckingham, M. P. Bogaard, D. A. Dunmur, C. P. Hobbs, and B. J. Orr, *Trans. Faraday Soc.* **66**, 1548 (1970).

^cAll processes are defined in the footnote of Table II.

^dReference 4.

TDHF percentage correction to the correlated static results [MBPT(2) and CCSD] for dc-SHG gives 1300 and 1200 a.u., respectively, while triples as measured by CCSD(T) give 1300 a.u., and are in good agreement with the experimental value of 1332 ± 15 a.u. The theoretical estimates for THG of 1500, 1400, and 1500 a.u. are lower than the experimental mean value, 1860 ± 270 a.u. but nearly fall within the rather large error bars. The other correlated [SDQ(4)] study of the hyperpolarizability of CO_2 ^{9(b)} gives for static γ_{\parallel} 1197 a.u. compared to our 1150 a.u., showing excellent agreement. Our results suggest the triples would likely increase that value by 7%. For CO_2 , the γ_{vib} has also been determined to be -86.83 at $\omega=0.07$ a.u. for dc-SHG and $+2.0$ a.u. for THG.^{34,35}

N_2

The N_2 results are shown in Table III. The behavior is quite similar to that for CO_2 . At the SCF [i.e., TDHF($\omega=0$)] level we obtain $\bar{\alpha}=11.42$ compared to 11.40 obtained in a $(6s5p3d2f)$ basis^{46(b)} and 11.57^{9(a)} in a $(6s4p3d1f)$ basis. Our SCF $\Delta\alpha$ of 5.37 compares reasonably to 5.11 and 5.17 from those calculations. As we introduce correlation our $\bar{\alpha}$ increases to be in good agreement with experiment, while $\Delta\alpha$ appropriately decreases. Other SDT-MBPT results behave differently increasing $\Delta\alpha$ to 5.48.⁴⁶ It should be noted, however, that this particular MBPT approach presents a diagrammatic evaluation of second-order *property* diagrams (see Ref. 47 for a discussion) and is not equivalent to the results from a finite-field energy derivative approach which would introduce a larger selection of correlation contributions. In particular, using the latter, SDQ(4) gives 4.65.^{9(a)}

The static γ_{\parallel} SCF value is 730 a.u. Correlation effects increase this by up to 40%, with triples being 6% of the value, compared to 7% for CO_2 . In the CO_2 case, CCSD reduces the MBPT(2) γ_{\parallel} instead of enhancing it. The 950

a.u. CCSD value is in reasonable agreement with the SDQ(4) value of 830.^{9(a)} Like correlation, TDHF dispersion effects show a similar increment of 3% to 30% of the static values, in the usual order THG > dc-SHG > IDRI > EKE. Introducing correlation and dispersion, reasonable agreement with THG experiment is obtained, although unlike CO_2 there is somewhat more error for dc-SHG. Results for optical properties at several different frequencies are presented elsewhere.¹⁶

H_2

The polarizabilities and the static second hyperpolarizabilities of H_2 are presented in Table IV. As our results are only for the electronic part, we compare with the exact electronic results taken from the very accurate explicitly correlated calculation of Bishop *et al.*,⁴⁸ where the additional vibrational effects are also presented. Our relatively poor agreement with the exact electronic results requires some basis set extension. For example, the calculated ratios $\gamma_{zzzz}/\gamma_{xxxx}$ with basis set 1 are more than 3. By adding the diffuse polarization (d -function exponent 0.1), γ_{zzzz} decreases, while γ_{xxxx} increases and the ratio of the two components becomes close to one. The γ_{xxzz} component seems to be less sensitive to the choice of basis set. The same tendency in the improvement of the hyperpolarizability components was observed in a previous study.²⁶ Similarly, even the polarizability and anisotropy show improvement from basis set 1 to basis set 2. Basis set 2, despite its relatively modest size, provides the parallel component $\gamma_{\parallel}=610$ that is comparable to the exact theoretical calculation at the static limit, 613.2.⁴⁸ For dc-SHG at $\lambda=694.3$ nm TDHF dispersion correction increases our static value to 706.4 a.u. The corresponding value calculated from the exact components is 721.2 a.u. Thus the percentage correction for the dispersion effect of 15.8% by TDHF is slightly lower than that obtained by the exact calculation (17.6%). This seems to be typical of TDHF as a measure of dispersion, as it usually obtains the correct effect at standard frequencies to within a couple of percent, barring pathological cases. TDHF or even any correlated treatment of dispersion, will certainly fail near a resonance. TDHF=RPA is also known to generally provide reasonable singlet excitation energies, which is necessary if it is to give a good dispersion estimate.

Table IV shows the correlated γ_{\parallel} for the various processes after correction for the dispersion. The correlated results such as MBPT(2) and CCSD (full CI for H_2) are improved and close to the exact results. After averaging over the vibrational zero-point wave function the exact γ_{\parallel} becomes 682.7 a.u. at the static limit and 811.6 a.u. at $\lambda=694.3$ nm for dc-SHG. This is a part of the vibrational effects. The other so-called "pure" vibrational contribution γ_{vib} (i.e., the part that involves scattering through vibronic states³) to γ_{\parallel} is a large $+183.7$ a.u. at the static limit,^{3,32,33} while the more appropriate frequency dependent value is a smaller -13.5 a.u. at $\lambda=694.3$ nm. This results in a γ_{\parallel} of 866.4 and 798.1 a.u., respectively.⁴⁸ As can be easily seen from the actual calculations⁴⁸ no percentage dispersion correction can be applied for γ_{vib} . The importance of γ_{vib} is

TABLE IV. Components of the polarizability and second hyperpolarizabilities^a of the H₂ molecule and results for various processes (in a.u.).

	SCF/ TDHF	MBPT(2)	CCSD	Exact ^b	EXP
$\alpha_{xx} = \alpha_{yy}$	4.3940	4.3655	4.3423		
	4.6199	4.6081	4.5969	4.5786	
α_{zz}	6.5481	6.5693	6.5640		
	6.4453	6.4846	6.4929	6.3875	
$\bar{\alpha}$	5.112	5.100	5.082		
	5.228	5.234	5.223	5.1816	5.43 ^c
$\Delta\alpha$	2.154	2.204	2.222		
	1.825	1.877	1.906	2.0371	2.035 ^d
γ_{xxxx}	240.0	260.0	270.0		
	530.0	580.0	590.0	575.9	
γ_{zzzz}	760.0	800.0	810.0		
	560.0	620.0	630.0	682.5	
γ_{xxzz}	220.0	230.0	230.0		
	200.0	210.0	210.0	211.9	
γ_{\parallel}	450.0	480.0	490.0		
	550.0	600.0	610.0	613.2	
THG	631.0	670.0 ^f	680.0 ^f		
	747.0	810.0	830.0	858.0 ^f	950 ± 140 ^e
dc-SHG	530.0	560.0	570.0		
	639.0	690.0	710.0	721.0	801 ± 4.5 ^e
IDRI	505.0	530.0	540.0		
	607.0	660.0	670.0		
EOKE	478.0	510.0	520.0		
	578.0	630.0	640.0	646.0	560 ± 60 ^e

^aThe upper and lower numbers are obtained by the calculations using basis set 1; [3s2p] and basis set 2; [3s2p1d] (*d* function on hydrogen has exponent 0.1).

^bThe numbers are evaluated by the formulas in the footnotes c–e in Table II using the pure electronic values from Ref. 48.

^cA. C. Newell and R. C. Baird, *J. Appl. Phys.* **36**, 3751 (1965).

^dK. B. MacAdam and N. F. Ramsay, *Phys. Rev. A* **6**, 898 (1972).

^eThe experimental values are from D. P. Shelton, *Phys. Rev. A* **42**, 2578 (1990), and include vibrational effects in addition to the electronic contributions. See the text.

^fSee footnote g, Table II.

process dependent, but it is quite small for the frequencies and processes we study here. The rather large vibrational correction of −13.5 a.u. in this case is peculiar to H₂. Of course, vibrational effects in all H-containing molecules would be expected to be comparatively significant. Allowing for corrections, the computed theoretical numbers obtained in basis 2 are reasonably close to the exact values; thus we decided to use this H-basis set for a systematic study of hyperpolarizabilities of larger H-containing molecules.

C₂H₄

Ethylene is the first of the linear polyene series whose nonlinear optical behavior provides a reference point for the development of optical polymer materials. The components of the polarizability, α , and hyperpolarizability, γ , for C₂H₄ are shown in Table V. The results employ basis 2, that is the POL basis for C and H, with the latter augmented by the set of diffuse *d* functions found to be important in H₂. The extra Cartesian *d* functions introduce a linear dependence that requires removal to get adequately converged results. The agreement with experiment for $\bar{\alpha}$ and $\Delta\alpha$ is satisfactory, particularly allowing for slight dif-

TABLE V. Components of the polarizability and second hyperpolarizabilities of C₂H₄ and results for various processes (in a.u.).^a

	SCF/ TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
α_{xx}	36.373	34.034	33.834	33.854	
α_{yy}	24.622	25.341	24.934	25.148	
α_{zz}	23.064	22.853	22.033	22.239	
$\bar{\alpha}$	28.02	27.41	26.93	27.08	28.70 ^b
$\Delta\alpha$	12.60	10.17	10.65	10.47	10.98 ^b
γ_{xxxx}	3 300.0	6 100.0	5 400.0	5 600.0	
γ_{yyyy}	2 800.0	3 500.0	3 200.0	3 400.0	
γ_{zzzz}	11 900.0	11 800.0	9 800.0	10 200.0	
γ_{xxzz}	3 100.0	3 500.0	2 900.0	3 000.0	
γ_{yyzz}	2 500.0	2 600.0	2 200.0	2 300.0	
γ_{xyxy}	1 600.0	2 000.0	1 800.0	1 900.0	
γ_{\parallel}	6 500.0	7 500.0	6 400.0	6 700.0	
THG	17 500.0	20 300.0	17 300.0	18 200.0	
dc-SHG	9 900.0	11 400.0	9 700.0	10 200.0	9030 ± 200 ^c
IDRI	8 500.0	9 800.0	8 400.0	8 800.0	
EOKE	7 400.0	8 600.0	7 300.0	7 700.0	

^aThe *x* axis is the principal axis of the molecule, the *y* axis is in the plane and the *z* axis is out of the plane of the molecule. Basis set 2.

^bT. K. Bose and R. H. Cole, *J. Chem. Phys.* **54**, 3829 (1971).

^cReference 5.

ferences from our vibrationless results and the experimental values that are obtained including zero-point effects.

Introducing the frequency dependence (Table V), the TDHF result is in reasonable agreement with the dc-SHG experimental value. However, MBPT(2) increases the value significantly. As occurs in CO₂, the infinite-order CCSD method decreases the second-order result, and in this case, even to a value less than the TDHF result. Triple excitations increase the value slightly leaving the final dc-SHG result in excess of experiment by 13.4%. The correlation effects in ethylene are the smallest we have seen. They are larger in *trans*-butadiene,^{16,17} the next member of the polyene series. The other optical processes show similar behavior. This is the one example we have seen where MBPT(2) significantly overestimates the correlation corrections to the hyperpolarizability. Larger basis studies are warranted.

CO

The CO molecule has a β hyperpolarizability along with γ . These are shown in Tables VI and VII. Along with β , we also report μ_z , which, because of its small value changes sign from the SCF value. For μ_z , CCSD provides excellent agreement with the experimental value although including triple excitations via CCSD(T) hurts the agreement. Slight basis set changes will affect the dipole moment in the third decimal. For the polarizability, many extensive basis set calculations have been reported, and are well summarized by Rijks and Wormer.⁴⁹ Our result for $\bar{\alpha}$ is in excellent agreement with the vibrationally corrected experimental result quoted by Werner and Meyer.⁵⁰ The anisotropy, as usual, is somewhat poorer but consistent with Werner and Meyer's CEPA value of 3.91. Sunil and Jordan⁵¹ get 3.79 using CCD.

TABLE VI. Dipole moment and components of the first hyperpolarizabilities of the CO molecule and results for various processes (in a.u.).

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
μ_z	-0.0989	+0.1208	+0.0421	+0.0581	+0.044 ^c
β_{zzz}^a	(-)28.2	25.6	26.1	26.0	
β_{zzx}	(-)3.5	6.0	6.1	6.6	
β_{zzx}^b	(-)21.1	22.6	23.0	23.5	
SHG ^d	24.1	25.9	26.4	27.0	29.9 ± 3.2 ^e
OR or	21.9	23.6	24.1	24.6	
EOPE ^f					

^aThe z axis is the principal axis of the molecule.^b $\beta_{ijl} = (\beta_{ijl} + \beta_{jil} + \beta_{lji})/5$ with summation convention.^cReference 50, and references therein.^dSHG: second harmonic generation, $\beta(-2\omega; \omega, \omega)$.^eReference 4. Since $\chi^{(2)} = \beta/2$ conversion factor is $\frac{1}{2} \times 8.639 \times 10^{-11} = 4.3195 \times 10^{-11}$ esu/molecule/a.u.^fOR: optical rectification, $\beta(0; \omega, -\omega)$. EOPE: electro-optic Pockels effect, $\beta(-\omega; \omega, 0)$. After averaging these two are numerically equal.

Discussing the $\gamma_{||}$ hyperpolarizability first we see some similarities with CO₂ and N₂. The static $\gamma_{||}$ value is increased via electron correlation by up to 57%. Like CO₂, and unlike N₂, the infinite-order correlation effects measured by CCSD slightly reduce the correlation correction, while triples further enhance it. The 7% effect of triples is consistent with that observed for N₂ and CO₂. TDHF dispersion varies from 6% for EOKE to 47% for THG. Combining dispersion and correlation, the dc-SHG result is slightly too large compared to experiment as is that for N₂.

The first (β) hyperpolarizability with dispersion allows the evaluation of second harmonic generation, $\beta(-2\omega; \omega, \omega)$ (SHG); optical rectification, $\beta(0; \omega, -\omega)$ (OR); or the electro-optic Pockels effect, $\beta(-\omega; \omega, 0)$ (EOPE). For $\beta_{||} = (\beta_{ijj} + \beta_{jij} + \beta_{jji})/5$ (summation convention) the latter two are numerically equivalent. Unlike γ , β has a sign, and is defined to be positive when the

product $\beta \cdot \mu$ is positive, that is when it has the same direction as the dipole moment. The evaluation of β is simpler than γ in the sense that it is a lower-order (third-order) quantity in the electric field, and only requires a knowledge of the first-order perturbed wave function if the usual $2n+1$ rule of perturbation theory is used. However, it is more complicated in the sense that it depends upon delicate, relative differences in the molecule's charge density, causing it to be more sensitive to different basis set characteristics than is γ .

Since the dipole moment of CO is known to have the wrong sign at the SCF level, which is corrected once an adequate amount of electron correlation is included, the SCF value of $\beta_{||}$ must have the opposite sign to μ_{SCF} , but the same sign once correlation is introduced. This is what we see as indicated by the (-) sign in the SCF column of Table VI. In other words the sign of $\beta_{||}^{SCF}$ is correct even though that of μ_{SCF} is not.

The correlation corrections to $\beta_{||}$ show a more modest increase than was observed for $\gamma_{||}$, being 11% of the static value at the CCSD(T) level. Dispersion also increases the result by 4.4% for OR and up to 14% for SHG. Combining the dispersion and correlation effects, for this relatively nonpolar molecule, the agreement with experiment for SHG is quite good. The basis set is certainly not converged, however, and extensions might change the degree of agreement.

HF

In Tables VIII and IX, we present the dipole moment, polarizabilities, and hyperpolarizabilities of the FH molecule. Values are reported for each component in three different basis sets. The first is for Sadlej's standard POL basis³⁶ (basis set 1), which appears to have adequately described the $\gamma_{||}$ hyperpolarizability for N₂, CO, and CO₂. The second adds the diffuse *d* polarization function on hydrogen (basis set 2), which was important in H₂. To potentially introduce a dramatic change compared to the nine rather extensive (*s,p,d,f*) conventional basis sets considered by us previously^{6,8} and other even more extended, atom centered basis sets considered by others,^{14,31} we choose to introduce three sets of lone-pair functions (one *s* and a set of *p* functions for each lone pair) to basis set 2 to define (basis set 3). As may be observed in Table VIII, for the dipole moment the improvement is negligible for both extensions, but for $\beta_{||}$ both effects are significant. At the SCF level each extension has comparable importance, but the synergistic effect with correlation is even more dramatic. The first extension causes about an 18% CCSD increase while the second adds another 8%. The net effect is a 24% increase in $|\beta_{||}|$ from that obtained with just the POL basis. Once again, the effect of triple excitations as measured by CCSD(T) slightly hurts the (probably fortuitous) agreement with experiment of CCSD for the dipole moment. We should always recognize, however, that the perturbative (T) correction, though generally good, is not necessarily the correct measure of triples, as it contains only one of five fifth-order contributions involving triples and connected quadruples that have about the same mag-

TABLE VII. Components of the polarizability and second hyperpolarizabilities of the CO molecule and results for various processes (in a.u.).^a

	SCF/ TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
α_{xx}	11.1068	11.7888	11.5997	11.7332	
α_{yy}	14.4752	15.7020	15.5647	15.6522	
$\bar{\alpha}$	12.23	13.09	12.92	13.04	13.08 ^b
$\Delta\alpha$	3.37	3.91	3.97	3.92	3.65 ^c
γ_{xxxx}	920.0	1380.0	1360.0	1470.0	
γ_{yyyy}	1200.0	1740.0	1740.0	1880.0	
γ_{zzzz}	360.0	520.0	510.0	540.0	
$\gamma_{ }$	1020.0	1500.0	1480.0	1590.0	
THG ^d	1484.0	2200.0	2200.0	2300.0	
dc-SHG	1211.0	1800.0	1800.0	1900.0	1720 ± 48 ^e
IDRI	1138.0	1700.0	1700.0	1800.0	
EOKE or	1071.0	1600.0	1600.0	1700.0	
OR					

^aThe z axis is the principal axis of the molecule.^bReference 50, includes zero-point ground state vibrational correction.^cG. H. F. Diercksen, B. O. Roos, and A. J. Sadlej, Chem. Phys. 59, 29 (1981).^dAll quantities are defined in the footnote in Table II, and correlated results incorporate the percentage TDHF dispersion correction.^eReference 4.

TABLE VIII. Dipole moment and components of the first hyperpolarizabilities of the HF molecule and results for various processes (in a.u.)^a

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
μ_z	0.7566 ^a	0.7079	0.7065		
	0.7570 ^b	0.7082	0.7070		
	0.7564 ^c	0.7069	0.7062	0.7008	0.708 ^d
β_{zzz}	-8.14	-8.80	-8.91		
	-8.15	-8.96	-9.02		
	-8.40	-9.10	-9.24	-9.62	
β_{zzx}	-0.26	-0.23	-0.08		
	-0.02	-1.03	-0.79		
	-0.28	-1.25	-1.03	-1.27	
$\beta_{ }$	-4.58	-5.56	-5.44		
	-4.87	-6.61	-6.36		
	-5.38	-6.96	-6.78	-7.30	
SHG	-5.024	-6.1	-6.0		
	-5.359	-7.3	-7.0		
	-5.853	-7.6	-7.4	-8.0	-10.9 ± 0.95 ^e
OR or	-4.711	-5.7	-5.6		
EOPE	-5.018	-6.8	-6.6		
	-5.522	-7.2	-7.0	-7.5	

^aBasis set 1; [5s3p2d/3s2p].^bBasis set 2; [5s3p2d/3s2p1d], the *d* function on hydrogen has an exponent of 0.1.^cBasis set 3; Basis set 2 plus lone-pair functions of *s* and *p* types with exponent=0.1 at 0.916 946 Å from fluorine.^dReference 50.^eReference 56.

nitude,⁴⁰ and even higher-order contributions will have a rôle in definitive answers. It is primarily an empirical observation that CCSD(T) generally works well for certain classes of problems,⁵² but it can fail in others.^{40,53}

From Table IX, a similarly modest change with basis in $\bar{\alpha}$ and $\Delta\alpha$ is observed. All three basis sets give effectively perfect agreement with other large basis SCF results for $\bar{\alpha}$ and for $\Delta\alpha$,^{49,54} and give rather consistent results at all correlated levels. The anisotropy of 1.10 does not compare well to experiment, or with some other correlated calculations that give values that include 1.16 (MCSCF⁵⁵), 1.27 (CEPA⁵⁰), and 1.37 from our older SDQ-MBPT(4) results.⁶ However, the CCSD, CCSD+T(CCSD), and CCSD(T) results of Chong and Langhoff¹⁴ with an extensive ANO basis give 1.18, 1.15, and 1.16, respectively, and 1.18 for MCPF, which are closer to the current value.

The change with basis is much more pronounced in $\gamma_{||}$, particularly for the γ_{xxxx} component, which increases by about 100 a.u. in SCF and about 200 a.u. in correlated calculations. The results with basis set 3 for $\beta_{||}$ and $\gamma_{||}$ are comparable or even larger in magnitude than those with the largest basis sets presented in our previous work,^{6,8} but there is still considerable difference from experiment.⁵⁶ A detailed assessment of the present results and comparisons with other results, including new atom centered basis results, will be considered in the Discussion section.

H₂O

Previously, we presented correlated SDQ-MBPT(4) results for H₂O in several different basis sets,⁷ including a (6s5p4d/4s2p) basis (*D*). In Tables X and XI, we summarize the dipole moment, polarizabilities, and hyperpolariz-

TABLE IX. Components of the polarizability and second hyperpolarizabilities of the HF molecule and results for various processes (in a.u.)

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
$\alpha_{xx} = \alpha_{yy}$	4.4567	5.3071	5.1636		
	4.4764	5.3508	5.1996		
	4.5103	5.3975	5.2390	5.3398	5.08 ^a
α_{zz}	5.7416	6.4072	6.3268		
	5.7758	6.4572	6.3681		
	5.7577	6.4326	6.3440	6.4378	6.40 ^a
$\bar{\alpha}$	4.89	5.67	5.55		
	4.91	5.72	5.59		
	4.93	5.74	5.61	5.71	5.52 ^a
$\Delta\alpha$	1.28	1.10	1.16		
	1.30	1.11	1.17		
	1.25	1.04	1.11	1.10	1.32 ^a
γ_{xxxx}	250.0	430.0	410.0		
	280.0	500.0	470.0		
	350.0	640.0	600.0	650.0	
γ_{zzzz}	250.0	340.0	320.0		
	280.0	380.0	370.0		
	270.0	380.0	360.0	390.0	
γ_{xxzz}	70.0	120.0	110.0		
	90.0	160.0	150.0		
	100.0	170.0	160.0	180.0	
$\gamma_{ }$	240.0	390.0	370.0		
	280.0	470.0	440.0		
	320.0	560.0	520.0	560.0	
THG	303.0	490.0	470.0		
	347.0	590.0	550.0		
	404.0	700.0	660.0	710.0	
dc-SHG	270.0	440.0	420.0		830 ± 120 ^b
	308.0	520.0	490.0		
	359.0	620.0	580.0	630.0	
IDRI	260.0	420.0	400.0		
	297.0	500.0	470.0		
	345.0	600.0	560.0	610.0	
EOKE or	251.0	410.0	390.0		
dcOR	286.0	480.0	460.0		
	333.0	580.0	540.0	590.0	

^aG. H. F. Diercksen and A. J. Sadlej, *J. Chem. Phys.* **75**, 1253 (1981). Experimental values with zero-point vibrational corrections.^bReference 54.

abilities of H₂O in the standard POL basis 1 and basis 3. The two sets of lone-pair functions to H₂O (basis set 3) are located at the normal OH distance but directed symmetrically away to help in the description of the lone pairs on O (see Table I for lone-pair basis orientation). We also investigated locating the lone-pair functions at the covalent radius of O but there were no important changes. Compared to the older basis *D* results, there is little change in SCF μ_z or $\bar{\alpha}$ with either basis. Here CCSD(T) gives a slightly better μ_z than does CCSD. The very small anisotropy, $\Delta\alpha$, is off from experiment by almost a factor of 2. The MBPT(4) anisotropy from Maroulis^{13(a)} is a similar 0.32, while that of Diercksen and Sadlej is 0.45.⁵⁷

The components which have small amplitudes such as β_{zzx} of H₂O are very sensitive to the choice of basis sets, but, typically, $\beta_{||}$ itself is not as sensitive as some of its components. The SCF $\beta_{||}$ was -9.2 a.u. in basis *D*. Similarly, SDQ-MBPT(4) results for basis *D* gave -13.7 for $\beta_{||}$ falling between the current POL values and those for

TABLE X. Dipole moment and components of the first hyperpolarizabilities of the H₂O molecule and results for various processes^a (in a.u.).

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
μ_z	0.7804 ^b 0.7793 ^c	0.7297 0.7272	0.7287 0.7273	0.7196	0.721 ^d
β_{zzz}	-4.6 -7.1	-8.7 -13.7	-7.3 -12.0	-13.7	
β_{zzx}	-0.6 -1.4	-2.4 -5.9	-2.0 -5.2	-6.2	
β_{zyy}	-9.7 -9.4	-10.6 -9.4	-10.8 -9.9	-10.2	
β_{\parallel}	-8.3 -10.8	-13.0 -17.5	-12.1 -16.2	-18.0	
SHG	-9.860 -12.568	-15.5 -20.4	-14.5 -19.0	-21.1	-22 ± 6 ^e
OR or EOPE	-8.727 -11.290	-13.8 -18.4	-12.8 -17.1	-19.0	

^aThe z axis is the principal axis of the molecule.^bBasis set 1; [5s3p2d/3s2p].^cBasis set 3; [5s3p2d/3s2p1d] plus two s,p lone pair functions (exp. 0.1).^dReference 50.^eReference 4.

basis set 3. The present lone-pair static hyperpolarizabilities are close to the static values obtained by Maroulis^{13(a)} with a large (8s6p5d2f/4s4p2d) basis set. At the SCF level his β components are -9.4, -7.6, and -1.3 and give a β_{\parallel} of -11.0, all of which are in excellent agreement with our results. At the MBPT(2) level $\beta_{\parallel} = -17.3$, compared to our -17.5 value. In a somewhat smaller basis (W1) he obtains a fourth-order triple contribution to β_{\parallel} of -2.7 a.u. compared to our CCSD(T) measure of -1.8 a.u. It is customary for fourth order to overestimate the real triple excitation effects, which are better estimated by T(CCSD) or the (T) correction. The theoretical estimate of both hyperpolarizabilities after the dispersion correction provides good agreement with experiment for H₂O.

NH₃

Lazzeretti and Zanasi (LN)⁵⁸ report the dipole moment, polarizability and the static first hyperpolarizability of NH₃ at the SCF level while Liu and Dykstra (LD)⁵⁹ also report SCF static first and second hyperpolarizabilities. The LN results in a (4s6p3d1f/6s2p1d) basis are consistent for $\bar{\alpha}$ and $\Delta\alpha$ with values of 12.9 and 0.511, respectively. The LD results are 12.64 and 0.55. Maroulis (M)^{13(b),13(c)} reports 12.93 and 0.49 in his largest basis (7s5p5d2f/5s3p1d) which are in excellent agreement with our results (Tables XII and XIII). Maroulis' dipole moment is also in somewhat better agreement with ours, being 0.639 compared to our 0.637, while the value is 0.649 for LZ and 0.642 for LD. We see a more dramatic change in β_{\parallel} where LN get 12.86, LD 14.84, and Maroulis 15.99, compared to our SCF basis 3 value of 15.1. For the individual tensor elements, our β_{zzz} value of 11.1 differs substantially from the LN value of 7.8 and the LD value of 9.1. However, it is close to the M 11.8 value. For β_{zzx} our basis 3 value of 7.0 falls among the LN value of 6.8, the LD value of 7.8, and the M value of 7.4.

TABLE XI. Components of the polarizability and second hyperpolarizabilities of the H₂O molecule and results for various processes (in a.u.).

	SCF/ TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
α_{xx}	7.8428 7.9569			9.6362	
α_{yy}	9.1647 9.1645	10.0505 10.0352	9.8930 9.8730	10.0166	
α_{zz}	8.4993 8.5264	9.7503 9.8193	9.4881 9.5416	9.7285	
$\bar{\alpha}$	8.50 8.55	9.79 9.87	9.55 9.61	9.79	9.81 ^a
$\Delta\alpha$	1.14 1.05	0.42 0.25	0.56 0.41	0.34	0.661 ^a
γ_{xxxx}	1200.0 1500.0	2200.0 2800.0	2000.0 2700.0	2900.0	
γ_{yyyy}	470.0 550.0	630.0 820.0	590.0 760.0	820.0	
γ_{zzzz}	770.0 920.0	1200.0 1540.0	1100.0 1390.0	1500.0	
γ_{xxzz}	330.0 400.0	580.0 750.0	550.0 700.0	770.0	
γ_{yyzz}	280.0 280.0	420.0 430.0	400.0 410.0	440.0	
γ_{xxyy}	290.0 350.0	550.0 660.0	540.0 620.0	680.0	
γ_{\parallel}	850.0 1010.0	1400.0 1780.0	1300.0 1650.0	1800.0	
THG	1273.0 1515.0	2100.0 2700.0	2000.0 2500.0	2700.0	
dc-SHG	1025.0 1216.0	1700.0 2100.0	1600.0 2000.0	2200.0	2310 ± 120 ^a
IDRI	961.0 1139.0	1600.0 2000.0	1500.0 1900.0	2000.0	
EOKE or dcOR	904.0 1069.0	1500.0 1900.0	1400.0 1700.0	1900.0	

^aM. A. Spackman, J. Phys. Chem. 93, 7594 (1989), as obtained from analysis of several experiments.^bReference 4.

Considering γ , our SCF γ_{xxxx} is closely bracketed by that of LD, 1070 and the 1297 value of M. γ_{xxxx} is the same to two digits in all calculations. Similarly our γ_{zzzz} of 4500 is again identical to two significant figures with M, while being only slightly larger than the LD value of 4300.

The correlation corrections are more than half of the total hyperpolarizability, emphasizing that the comparison to experiment at the SCF level is meaningless. The only other high-level correlated study of hyperpolarizabilities is the recent work of Maroulis.^{13(b),13(c)} In comparisons with his SDQ(4) results in a (6s4p4d1f/4s2p1d) basis, he obtains $\beta_{\parallel} = 30.47$ which is nearly identical to our results for CCSD, the infinite-order extension of SDQ(4). In a somewhat smaller basis he evaluates the fourth-order triples to contribute 4.42 a.u. to β_{\parallel} . We obtain 4.3 from the T evaluation in CCSD(T). Hence, all our results for β_{\parallel} are entirely consistent with those of M. Once TDHF dispersion is added, which is 43% for SHG (the largest we have obtained), our final CCSD(T) result falls within the experimental error bars. The other correlated result is limited to second order.¹⁸ At $\omega = 0.06$ a.u., their second-order SHG value is 40 and 45.3 at $\omega = 0.07$, in good agreement with the present results. Similarly, their OR value is 32.6 and

TABLE XII. Dipole moment and components of the first hyperpolarizabilities of the NH_3 molecule and results for various processes (in a.u.)^{a,†}

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
μ_z	0.6364	0.5994	0.5974		
	0.6369	0.5991	0.5976	0.5901	0.578 ^c
β_{zzz}	-6.4	-30.2	-26.4		
	-11.1	-37.8	-33.3	-39.6	
β_{zzx}	-6.8	-7.7	-7.6		
	-7.0	-8.1	-8.0	-8.8	
β_{ij}	-12.1	-27.4	-25.0		
	-15.1	-32.5	-30.0	-34.3	
SHG	-17.946	-41.0	-37.3		
	-21.978	-46.6	-42.5	-49.1	-48.4 ± 1.2 ^d
OR or	-13.595	-31.0	-28.3		
EOPE	-16.740	-36.3	-33.1	-38.3	

^a z is the principal axis of the molecule.[†]First number is from basis set 1; second from basis set 3.^cW. H. Weber, J. Mol. Spectrosc. 107, 405 (1984).^dReference 4.

33.9 at the respective frequencies. As the comparable TDHF percentage dispersion effect is virtually identical to that obtained in a second-order correlated dispersion calculation,¹⁸ our final CCSD(T) results should be an excellent estimate. Vibrational corrections would be expected to increase the magnitude of the theoretical values somewhat.

For the correlated second hyperpolarizability, we again have consistency between the present basis 3 results and those of Maroulis. The latter SDQ(4) result of 3864 is again nearly identical to our CCSD 3800 value. Also, the T4 estimate in a smaller basis of 311 is in line with our

correction of 400, so that his estimated MBPT(4) results in his (6s4p4d1f/4s2p1d) basis would be virtually identical to our current basis 3, CCSD(T) results. Including dispersion, which is 40% for dc-SHG results we obtain good (8%) agreement with experiment. In this example, the POL basis is not too bad, itself, primarily only underestimating the β_{zzz} element significantly. The MBPT(2) values are slightly larger than CCSD values and in better agreement with experiment for both the H_2O and NH_3 molecules. It should be noted, however, that inclusion of triple excitations in general brings the CCSD hyperpolarizabilities back to a value close to that for MBPT(2).

H_2S

H_2S is a molecule that is chemically and structurally quite different from H_2O . It involves a second-row atom, and has an HSH angle of 92.2°. The dipole moment, polarizabilities, and hyperpolarizabilities of H_2S are summarized in Tables XIV and XV with all three basis sets. The first hyperpolarizability is one of the smallest among the molecules studied here and therefore a very careful treatment is necessary even in the prediction of its sign. For example the SCF values obtained here have an opposite sign to that of experiment. The correlated calculation predicts the same sign as the experiment, but rather different values for different basis set choices. Once again the dipole moment and polarizability seem to be adequate in any of our three bases, and the CCSD μ_z is slightly better than that given by CCSD(T). However, a dramatic change is seen in the hyperpolarizabilities in the results between the

TABLE XIII. Components of the polarizability and second hyperpolarizabilities of the NH_3 molecule and results for various processes (in a.u.)^a

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
$\alpha_{xx} = \alpha_{yy}$	12.763	13.779	13.536		
	12.7683	13.7733	13.5280	13.7068	
α_z	13.279	15.711	15.242		
	13.3475	15.8334	15.3346	15.7139	
$\bar{\alpha}$	12.94	14.42	14.10		
	12.96	14.46	14.13	14.38	14.56 ^a
$\Delta\alpha$	0.52	1.93	1.71		
	0.58	2.06	1.81	2.01	1.94 ^b
γ_{xxxx}	1100.0	1500.0	1400.0		
	1200.0	1800.0	1700.0	1800.0	
γ_{zzzz}	4200.0	7300.0	6900.0		
	4500.0	8000.0	7400.0	8200.0	
γ_{xxzz}	1100.0	1800.0	1700.0		
	1100.0	1900.0	1800.0	2000.0	
γ_{ij}	2300.0	3700.0	3500.0		
	2400.0	4100.0	3800.0	4200.0	
THG	4590.0	7400.0	7000.0		
	4925.0	8300.0	7800.0	8500.0	
dc-SHG	3072.0	5000.0	4700.0		
	3276.0	5500.0	5200.0	5600.0	6090 ± 110 ^c
IDRI	2762.0	4500.0	4200.0		
	2937.0	5000.0	4600.0	5100.0	
OKE or dcOR	2501.0	4100.0	3800.0		
	2652.0	4500.0	4200.0	4600.0	

^aG. D. Zeiss and W. J. Meath, Mol. Phys. 33, 1155 (1977).^bN. J. Bridge and A. D. Buckingham, Proc. R. Soc. London Ser. A 295, 334 (1966).^cReference 4.

TABLE XIV Dipole moment and components of the first hyperpolarizabilities of the H₂S molecule and results for various processes (in a.u.)^a

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
μ_z	0.4375	0.4053	0.3924		
	0.4389	0.4029	0.3925	0.3834	
	0.4384	0.4037	0.3927	0.3850	0.401 ^b
β_{zzz}	11.3	6.2	7.7		
	6.8	-1.8	0.8	-0.7	
	7.9	6.2	2.6	1.1	
β_{zzx}	8.2	-2.0	-1.2		
	6.2	-5.5	-2.1	-4.2	
	5.5	-5.5	-2.2	-4.4	
β_{zxx}	11.6	-11.4	-11.7		
	-10.7	-10.2	-10.6	-10.6	
	-9.9	-9.2	-9.5	-9.5	
β	4.7	-4.4	-1.7		
	1.3	-10.5	-7.1	-9.3	
	2.2	-8.8	-5.5	-7.7	
SHG	5.813	-5.5	-2.1		
	1.488	-11.6	-7.9	-10.3	
	2.380	-10.1	-6.4	-8.8	-9.95 ± 2.1 ^c
OR or	5.038	-4.8	-1.9		
EOPE	1.450	-11.3	-7.7	-10.0	
	2.212	-9.4	-5.9	-8.2	

^aResults are for basis 1, 2, and 3. z axis is principal axis of the molecule.^bR. E. Hilder and M. W. P. Strandberg, Phys. Rev. **83**, 575 (1951); C. A. Burns, J. Chem. Phys. **28**, 427 (1958); G. A. Burns, *ibid.* **31**, 1270 (1959).^cReference 4.

POL basis 1 and basis 2, due to the diffuse H *d* function in the latter. The addition of the lone pair functions does not necessarily improve the answer as there is still significant oscillation between basis 2 and basis 3. This may be partly due to the location of the lone pair functions which is rather different than for H₂O. Also, the effect of the additional electrons and the comparative degree of reliability of the starting POL basis for second-row atoms can also be a consideration. Basis 2 gives better agreement with experiment, but the oscillatory behavior suggests further basis set extensions should be considered before claiming convergence.

γ_z shows a more modest change with basis, but basis 3 moves the result in the wrong direction compared to the experimental value. There seems to be room for important basis set improvements, although generally contrary to our experience ($\gamma_{||}$ is larger with every basis set increase in this paper) γ_z seems to be overestimated in basis 3 compared to the dc-SHG experiment.

DISCUSSION

In Tables XVI and XVII, we summarize theoretical results of the first- and second-electric susceptibilities for the several small molecules studied in this paper, now in esu units as reported in the experimental papers (see footnotes to Tables II and VI for conversion factors). The electric susceptibilities are $\chi^{(2)} = \beta_z/2$ and $\chi^{(3)} = \gamma_z/6$. The basis sets used in this study are created systematically from polarizability-consistent basis sets³⁶ and are only of modest size. The intent is to provide a broad study for several molecules. Hence, no particular effort is made to obtain the hyperpolarizabilities of a specific molecule.

The results, taken as a whole, allow us to draw some general conclusions about hyperpolarizabilities of small molecules. For $\chi^{(2)}$ the static SCF results have an average error of 56% compared to the quoted experimental values, so at least for small molecules we should not expect SCF results to provide better than a factor of 2 agreement. For $\chi^{(3)}$ the error is a similar 43%. The average SHG TDHF frequency dependence for the ruby laser frequency of 21% improves $\chi^{(2)}$ results to a 48% error; i.e., for SHG the average dispersion is about 8% of experiment. The average dispersion for $\chi^{(3)}$ dc-SHG is a larger 26% (15% of experiment), reducing the average error for TDHF to 28%. Assuming the scaled TDHF dispersion approximation used throughout this paper, the addition of second-order correlation reduces the $\chi^{(2)}$ error to 11% of experiment, and if we exclude the FH example, whose experimental value we question, the error is 6%. The 37% effect of correlation on $\chi^{(2)}$ is about four times the 8% dispersion effect. For $\chi^{(3)}$, the MBPT(2) correlation effect is 18%, or slightly larger than the dc-SHG dispersion effect, reducing the residual error for $\chi^{(3)}$ to 10%. Hence, except for FH, in a reasonable basis TDHF dispersion weighted MBPT(2) gives an average error of 10% for $\chi^{(3)}$. The infinite-order correlation corrections introduced by CCSD actually diminish the effect of correlation somewhat (~8%) for $\chi^{(2)}$ although for $\chi^{(3)}$ CCSD and MBPT(2) have the same average error. Once triple excitations are included via CCSD(T), the average error for TDHF scaled dispersion CCSD(T) results is reduced to 10.7% for $\chi^{(2)}$ and 10.1% for $\chi^{(3)}$. Again the exclusion of FH for $\chi^{(2)}$ would reduce the average error to 6.4% for $\chi^{(2)}$. Triple excitations account for 10% for $\chi^{(2)}$, but less than 1% on average for $\chi^{(3)}$. Clearly, even larger basis sets will change the distribution of effects somewhat, but the level employed in the present calculations should be sufficiently high to be indicative of the various contributions. Finally, it appears that good basis set, correlated, frequency dependent results that are within about 10% of the experimental values are possible. Exclusion of any one of the above contributions, however, would destroy this degree of agreement. β_{zib} and γ_{zib} values are quite small in the SHG and dc-SHG cases.³⁴

Assuming adequate basis set convergence, the remaining primary uncertainty lies in the inevitable limitations in the treatment of correlation. For the current results this would particularly pertain to the role of triple excitations. CCSD(T), which is the noniterative approximation to CCSDT-1,⁶⁰ and has been found to mimic well full CCSDT in several cases for electronic energies and vibrational frequencies.^{52,53} As such it is generally better than the original noniterative CCSD + T(CCSD) method,⁶¹ which is equivalent through fourth order, but differs by a single fifth-order term, $\Delta E_{5T}^{(5)}$,⁴⁰ particularly in difficult, multireference cases. None of the current molecules are expected to exhibit any unusual multireference character, but an assessment of reliability of CCSD(T) for *electric properties* has not yet been made. Since |T(CCSD)| is normally greater than |(T)|, when the two triple estimates are close, the extra term matters little and we usually have confidence in the triple excitation estimate. However, for some cases,

TABLE XV Components of the polarizability and second hyperpolarizabilities of the H₂S molecule and results for various processes (in a.u.)^a

	SCF/TDHF	MBPT(2)	CCSD	CCSD(T)	EXP
α_{xx}	23.8050	25.1651	24.8842		
	23.8941	25.3435	25.0502	25.3649	
	23.8398	25.3537	25.0353	25.3597	
α_{yy}	23.6693	24.2252	23.9997		
	23.7052	24.3423	24.1097	24.2784	
	23.7556	24.4116	24.1738	24.3484	
α_{zz}	23.3747	24.2340	23.9832		
	23.4207	24.3808	24.1187	24.3251	
	23.4303	24.4539	24.1815	24.3969	
$\bar{\alpha}$	23.62	24.54	24.29		
	23.67	24.69	24.43	24.66	
	23.68	24.74	24.46	24.70	25.5, ^b 26.6 ^c
$\Delta\alpha$	0.38	0.94	0.89		
	0.41	0.98	0.94	1.06	
	0.37	0.92	0.86	0.99	
γ_{xxxx}	10 000.0	12 900.0	12 600.0		
	10 100.0	13 000.0	12 700.0	13 500.0	
	10 900.0	14 200.0	13 500.0	14 400.0	
γ_{xxyy}	2 100.0	2 600.0	2 500.0		
	2 500.0	3 200.0	3 000.0	3 200.0	
	2 600.0	3 300.0	3 200.0	3 400.0	
γ_{zzzz}	3 200.0	4 000.0	3 800.0		
	3 600.0	4 700.0	4 500.0	4 700.0	
	3 900.0	5 100.0	4 800.0	5 100.0	
γ_{xxzz}	2 300.0	3 000.0	2 900.0		
	2 400.0	3 300.0	3 100.0	3 300.0	
	2 600.0	3 500.0	3 300.0	3 500.0	
γ_{yyzz}	1 300.0	1 600.0	1 600.0		
	1 200.0	1 500.0	1 500.0	1 500.0	
	1 200.0	1 600.0	1 500.0	1 600.0	
γ_{xyxx}	2 200.0	2 800.0	2 700.0		
	2 400.0	3 200.0	3 100.0	3 300.0	
	2 400.0	3 300.0	3 100.0	3 300.0	
γ	5 400.0	6 900.0	6 700.0		
	5 700.0	7 400.0	7 100.0	7 500.0	
	6 000.0	7 800.0	7 500.0	7 900.0	
THG	13 429.0	17 200.0	16 700.0		
	14 290.0	18 700.0	18 000.0	19 000.0	
	15 223.0	20 200.0	19 300.0	20 000.0	
dc-SHG	7 815.0	10 000.0	9 700.0		
	8 275.0	10 800.0	10 400.0	11 000.0	
	8 713.0	11 600.0	11 000.0	11 700.0	10 300 ± 260 ^d
IDRI	6 840.0	8 700.0	8 500.0		
	7 221.0	9 500.0	9 100.0	9 600.0	
	7 573.0	10 100.0	9 600.0	10 200.0	
EOKE or	6 037.0	7 700.0	7 500.0		
dcOR	6 360.0	8 300.0	8 000.0	8 500.0	
	6 650.0	8 800.0	8 400.0	8 900.0	

^aResults are for basis 1, 2, and 3.^bJ. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 950.^cA. A. Maryott and F. Buckley, Nat. Bur. Stand. (U.S.) Circ. 537 (1953).^dReference 4.

though CCSD+T(CCSD) and CCSD(T) coincide, both can differ significantly from CCSDT.⁴⁰ In Table XVIII we compare CCSD+T(CCSD) and CCSD(T) for static hyperpolarizabilities.

For all cases but FH, the γ_{ij} values, retaining two significant digits, are essentially the same. For β_{ij} the average increase in magnitude is about 7% except for CO, which shows almost no change. Hence, we are confident of the triple estimate for these examples. Some small change

would occur in comparisons of β_{ij} with experiment for FH, H₂O, and NH₃ if we used T(CCSD), but since we tend to believe that T(CCSD) overestimates the triple correction, we prefer the CCSD(T) values. However, in the absence of full CI, or results from higher approximations like CCSDT⁶² or CCSD+Q,⁶³ we can be relatively (but not absolutely) certain that the triple excitation estimate in CCSD(T) will be reliable for quantities as sensitive as hyperpolarizabilities. Here except for the very small hyper-

TABLE XVI. Theoretical^a and experimental^b hyperpolarizabilities (10^{-32} esu/molecule) for SHG.

	MBPT(2)	CCSD	$\chi_{ }^{(2)} = \frac{1}{2}\beta_{ }^{\text{SHG}}$ CCSD(T)	Exp.
CO	11.2	11.4	11.7	12.9 ± 1.4
HF	-3.3	-3.2	-3.4	-4.70 ± 0.41
H ₂ O	-8.8	-8.2	-9.1	-9.4 ± 0.4
NH ₃	-20.1	-18.4	-21.2	-20.9 ± 0.5
H ₂ S	-4.4	-2.8	-3.8	-4.3 ± 0.9

^aValue corrected for the dispersion effect at 694.3 nm using the TDHF percentage dispersion correction. All the calculations are performed with basis sets [5s3p2d] for C, N, O, and F; [7s5p2d] for S; and [3s2p1d] for H. The lone-pair functions are added for HF, H₂O, NH₃, and H₂S. All molecules at experimental geometries and there is no estimate of vibrational corrections.

^bValue obtained by dc-induced second harmonic generation (Refs. 4, 5, and 56).

polarizabilities of FH, any difference with experiment due to triples estimates will not affect our 10% error.

Because of cancellation of errors, MBPT(2) can provide results for correlation that can be in accidentally better agreement with experiment than the theoretically more complete CCSD as the effect of triple excitations is generally to move CCSD closer to MBPT(2). This computationally useful observation is not universal, however, as the C₂H₄ example shows a significant MBPT(2) overestimate for $\chi_{||}^{(3)}$ compared to CCSD(T).

Because of the above conclusion that calculations at the level used here provide results to within a mean error of 10%, the FH example still appears anomalous, as it did in our earlier work.^{6,8} In basis 3, at r_e the CCSD(T) error is 28% for $\chi_{||}^{(2)}$ and 24% for $\chi_{||}^{(3)}$. Although not too great, they are about three and two times the next largest percent error, respectively. Compared just to H₂O and NH₃, the FH error is close to a factor of 10 for $\chi_{||}^{(2)}$ and 3 for $\chi_{||}^{(3)}$. Of course, FH can also have characteristics that are peculiar to it, which selectively reflect deficiencies in the approximate quantum chemical solutions employed, and any systematic error would be amplified in the percentage cor-

TABLE XVII. Theoretical^a versus experimental^b hyperpolarizabilities of the molecules (10^{-39} esu/molecule).

	MBPT(2)	CCSD	$\chi_{ }^{(3)} = \frac{1}{6}\gamma_{ }^{\text{dc-SHG}}$ CCSD(T)	Exp.
H ₂	58.2	59.3	59.3	60.5 (exact)
CO	151.0	149.0	160.0	144.0 ± 4.0
N ₂	88.7	90.6	96.0	86.6 ± 1.0
CO ₂	111.5	107.9	110.0	111.9 ± 1.3
C ₂ H ₄	960.0	820.0	860.0	758.0 ± 17.0
HF	52.0	49.0	53.0	70.0 ± 10.0
H ₂ O	180.0	170.0	180.0	194.0 ± 10.0
NH ₃	460.0	430.0	470.0	511.0 ± 9.0
H ₂ S	970.0	930.0	980.0	865.0 ± 22.0

^aAll the calculations are performed with basis sets [5s3p2d] for C, N, O, and F; [7s5p2d] for S; and [3s2p1d] for H. The lone-pair functions are added for HF, H₂O, NH₃, and H₂S. All molecules at experimental geometries and there is no estimate of vibrational corrections.

^bValue obtained by dc-induced second harmonic generation (Refs. 4, 5, and 56).

TABLE XVIII. Comparison of different noniterative triple excitation estimates for static hyperpolarizabilities (a.u.)

	β		γ	
	CCSD(T)	CCSD + T(CCSD)	CCSD(T)	CCSD + T(CCSD)
CO ₂			1100	1200
N ₂			1000	1000
C ₂ H ₄			6700	6700
CO	-23.5	-23.0	1600	1600
HF	-7.3	-7.8	560	610
H ₂ O	-18.0	-19.5	1800	1900
NH ₃	-34.3	-36.9	4200	4300
H ₂ S	-7.7	-8.3	7900	8000

rection since it has the smallest $|\chi^{(2)}|$ and $|\chi^{(3)}|$ of the three molecules. In other words, systematic errors that affect all calculations, will disproportionately cause a higher percentage error in a small value than in a large one. Hence, the molecule requires further consideration.

The original paper on FH (Ref. 6) used the SDQ-MBPT(4) method (the fourth-order approximation to CCSD) and computed static hyperpolarizabilities in several different, large polarized basis sets. The *D* (6s5p4d/5s3p) basis gave -2.83×10^{-32} esu/molecule for $\chi^{(2)}$ ($\omega=0$) at r_e and 39×10^{-39} esu/molecule for $\chi^{(3)}$ ($\omega=0$). These numbers should be compared with the current basis 3, CCSD static values which are -2.9 and 44 , respectively. In other words, even the rather drastic and unconventional basis set addition of lone pair functions has only had a modest effect on the original 1979 values. Comparison with the later 1986 results,⁸ namely, -2.79 and 37 , in basis *E* [i.e., (6s5p4d2 f/5s3p)] are again completely consistent. In basis *F*, we added a set of *d* functions on H, exponent 1.0, to the *E* basis to give (6s5p4d2 f/5s3p1d). Since we did not previously report correlated calculations in that basis, we do so here. At the CCSD level, basis *F* gives -2.8 and 37 esu for $10^{-32} \chi^{(2)}$ and $10^{-39} \chi^{(3)}$, respectively, and they are again consistent. The *F* basis MBPT(2) values are -2.9 and 41 . Further modification of bases *E* and *F* led to our basis *I*,⁸ namely, (6s5p4d2 f/5s3p), which had more diffuse *d* and *f* exponents. This basis gave a larger β_{xxz} element, and the functions in the basis have since been found to be important in the satisfaction of the dipole length and velocity equivalence in RPA calculations.⁶⁴ We previously only reported MBPT(2) calculations with basis *I*. Here, we take basis *I* and add the *d* function on H (exponent 1.0) to give what we will call basis *J* for consistency with the prior calculations, and do a full set of correlated calculations. In basis *J* CCSD values are 2.97 and 40 , and the MBPT(2) values 3.08 and 43 . The conclusion is that despite a variety of conventional and unconventional bases, our current static results differ rather insignificantly ($< 10\%$) from the original, static r_e values.

The first additional effect that more significantly changes the computed static values is the inclusion of triple excitation effects. This contribution in basis *E* causes the SDTQ-MBPT(4) values to be -3.13 and 43 , respectively. This is similarly observed in the current basis 3 results, whose values at the CCSD(T) level are -3.15 and 47 . The

TABLE XIX. Comparison of electric susceptibility results for FH from different calculations (esu/molecule)

Reference	Level	Basis	$10^{12}\chi^{(2)}(\omega=0)$	$10^{19}\chi^{(1)}(\omega=0)$	$10^{12}\chi^{(2)}(2\omega,0,0)^a$	$10^{19}\chi^{(1)}(2\omega,0,0,0)^a$
1979 BP (6)	SDQ-MBPT(4)	$D:(6s5p4d/5s3p)$	-2.83	39 ^b	-3.2 (-3.5) ^c	44(49) ^c
	MBPT(2)	"	-2.73	40 ^b	-3.04 (-3.20) ^d	44(45) ^d
1986 SB (8)	CCSD	$E:(5s5p4d2f/5s3p)$	-2.62	35		
	CCSD+T4	"	-2.97	41	-3.14 (-3.29) ^d	44(45) ^d
	MBPT(2)	"	-2.72	39		
	SDQ-MBPT(4)	"	-2.79	37		
	MBPT(4)	"	-3.13	43	-3.30 (-3.45) ^d	46(47) ^d
	MBPT(2)	$I:(6s5p5d1f/5s3p)$	-3.2	41		
	(CCSD+T4)	"	-3.5	44	-3.6 (-3.8) ^d	47(48) ^e
1990 CL (14)	MCPF	$(8s6p4d3f/5s3p2d)$	-3.12	43		
	CCSD	"	-2.89	39		
	CCSD(T)	"	-3.10	43		
1992 JJJ (28)	MCLR-CAS 4220 ^b	$(8s6p4d3f/5s3p2d)^f$	-2.80	37	-3.08 (-3.36) ^d	43
	MCLR-CAS 6331	"	-2.87			
1992 SB (present work)	CCSD(T)	$J:(6s5p5d1f/5s3p1d)$	-3.21	44	-3.49 (-3.65) ^d	49(50) ^d
	CCSD	"	-2.97	40		
	MBPT(2)	"	-3.07	43		
	CCSD(T)	$(5s3p2d/3s2p1d$ $//3x(1s,1p)$ lone pair)	-3.15	47	-3.43 (-3.59)	53(55)
	MBPT(2)	"	-3.01	47		
	CCSD	"	-2.93	44		
	CCSD(T)	Largest effects ^g	-3.26	47	-3.58 (-3.86)	56(57)
Experiment					(-4.70 ± 0.41)	(70 ± 10)

^a $\omega=0.0656$ a.u.^bReference 56 reports 35 by estimating γ_{vib} . Footnote 38(a) in the reference corrects this value to 39 using our computed value. F(1 σ^2) core correlation effects included.^cFirst line incorporates 14% dispersion and 10% zero-point correction as estimated by Dudley and Ward (Ref. 56), while the second value was obtained using actual TDHF percentage dispersion and computed vibrational average.^dVibrationally "averaged" results in (). Reference 31 finds a -0.28 unit effect for $\chi^{(2)}(-2\omega;\omega,\omega)$ due to zero-point average. SB found -0.15 at the static CCSD+T4 level in Ref. 8 and 1 unit for $\chi^{(1)}(0;0,0,0)$. In the new results we report values at $r_0=1.7621$ a.u. (Ref. 50) instead of r_e to partly incorporate this effect, getting -2.52 SCF, -3.14 MBPT(2), -3.09 CCSD, and -3.31 for CCSD(T). Similarly, the $r_0 10^{19}\chi^{(1)}(0;0,0,0)$ values are 28 SCF, 48 MBPT(2), 45 CCSD, and 49 for CCSD(T). These results are nearly identical to our previous zero-point averaged corrections from 1986 (Ref. 8).^eThis CCSD+T4 result from Ref. 8 was extrapolated from the MBPT(2) results for basis I, assuming all effects beyond MBPT(2) to be additive.^fThis ANO basis (Ref. 31) differs from that of Chong and Langhoff (Ref. 14).^gWe report results from the largest, computed static tensor elements from any of the above calculations (see the text) augmented with the largest observed zero-point vibration and dispersion effects from Jaszuński *et al.* (Ref. 31). The MCLR SHG dispersion is 10% and dc-SHG dispersion, 19%. This would seem to offer an upper bound to the magnitude of $\chi^{(2)}$ and $\chi^{(1)}$ as can be justified by all current high-level correlated calculations.

next important element is to average over the zero-point vibration.⁷ Here we approximate this average by evaluation at r_0 . With displacement β_{zzz} becomes -10.3 a.u. compared to -9.6 a.u. at r_e , while β_{zzx} is -1.26 a.u. instead of -1.27 a.u. at r_e . For CCSD(T) this changes $10^{12}\chi_{\parallel}^{(2)}$ to -3.31 and $10^{19}\chi_{\parallel}^{(1)}$ to 49. Finally, using the TDHF percentage dispersion, we obtain -3.59 and 55, respectively. If we go back and compare with our original 1979 results, including the upper bound 10% zero-point vibration correction and 14% dispersion correction estimated by Dudley and Ward,⁵⁶ we have -3.5 and 49, which is still in good agreement. Alternatively, we can use the actual vibration and dispersion correction we obtained⁸ to give the second set of values in Table XIX, which are slightly smaller in magnitude. So despite improvements in the calculation primarily due to the addition of triple excitations, the original values are still close to the best that we have since obtained. Hence, our current values seem to be well converged.

This conclusion is also supported by the other high-level correlated calculations that have been reported.

Chong and Langhoff¹⁴ use a more extensive atomic natural orbital (ANO) basis⁴⁴ (see Table XIX) and present a modified coupled pair functional (MCPF) calculation in addition to CC results. Their static values of -3.12 for $10^{12}\chi_{\parallel}^{(2)}$ and 43 for $10^{19}\chi_{\parallel}^{(1)}$ are in excellent agreement with all prior results that include triple excitations. Also, the CCSD(T) results are in excellent agreement with the MCPF values. As the ANO basis is generated from a different premise than the basis sets introduced in our work, the correspondence of results is indicative of a large degree of basis set convergence. Even the potentially drastic changes that are introduced via lone pair functions show little difference from the other results, contributing a maximum change of about 0.1 esu/molecule in $10^{12}\chi^{(2)}$ and 4 esu/molecule in $10^{19}\chi^{(1)}$.

The other high-level calculation reported for FH is that of Jaszuński *et al.*³¹ These authors report MCLR-CASSCF results. Their static correlated values are smaller in magnitude than those obtained by CCSD(T) methods, possibly due to the neglect of residual dynamic (i.e., CI) correlation. Their CASSCF results use very large CAS

configuration spaces of up to 125 000 determinants and perturbed CASSCF orbitals. In comparison, our J -basis CCSD(T) explicitly involves singles and doubles (~ 144 000 determinants and implicitly most of the effect of triples and quadruples!) with relaxed (i.e., coupled perturbed) Hartree-Fock orbitals. Their CASSCF results are close to our previous static SDQ-MBPT(4) and CCSD values and the CCSD values of Chong and Langhoff,¹⁴ but triple excitations enhance the prior values somewhat. Adding their zero-point vibrational average and dispersion, their final results remain quite close to those we obtained in basis E ,⁸ but are somewhat smaller in magnitude than the best current values. It should be noted that even very large CAS spaces do not necessarily introduce *all* appropriate dynamic correlation effects, frequently requiring the inclusion of CI on top of their CASSCF. This is reflected in their computed polarizabilities which have only 60% of the correlation effect. Any such dynamic correlation error in $\beta_{||}$ or $\gamma_{||}$ (and one would expect more in the latter because like $\bar{\alpha}$ it increases with molecular size), would modify their results to be close to the magnitude of the current, largest values. As it is, they obtain nearly the basis set E CCSD+T4 results of our paper.⁸ In that paper, we state that we believe the magnitude of $\chi_{||}^{(2)}$ will fall *between* our computed value of 3.3 and our *maximum* estimated value of 3.8. Their result of 3.36 falls within the specified range. It is likely that additional dynamic correlation will increase the magnitude of their computed values to be more in line with the current CCSD(T) results of 3.6 and 55.

To alleviate suspicion regarding any anomalous behavior of the lone pair basis set, we also report new CCSD(T) atom-centered basis results for basis set J . Previously, we recognized that the β_{zzx} tensor component for FH had been found to be larger in some of our other basis calculations than in our E basis results.⁸ This raised the question of a potential basis set deficiency in the perpendicular direction. To investigate this we considered several basis modifications that led to the I basis estimate made in our earlier paper⁸ whose MBPT(2) value for β_{zzx} was -1.6 compared to -0.7 in basis E . As the β_{zzx} component remained nearly the same, assuming the additivity of other effects, the larger MBPT(2) value for β_{zzx} in basis I led to a final, *maximum* estimate of -3.8 esu/molecule for $10^{32} \chi_{||}^{(2)}$. To better document the effects of this basis, we now report correlated results in basis J , which is I plus the set of Cartesian d (1.0 exponent) functions on H, i.e., (6s5p5d1f/5s3p1d). Though this is not that extensive a basis, our static CCSD(T) result of -3.21 is close to the lone pair basis results, while the $\chi_{||}^{(3)}$ value of 44 is slightly lower. After dispersion and vibration correction the results are -3.65 and 50 for $10^{32} \chi_{||}^{(2)}$ and $10^{39} \chi_{||}^{(3)}$ esu/molecule. At a given level of correlation, usually the more complete the basis the larger will be $\gamma_{||}$. If this applies here, the lone pair basis might be considered to be superior.

It is informative to estimate an upper bound for the magnitude of $\chi_{||}^{(2)}$ and $\chi_{||}^{(3)}$. For β_{zzx} , Chong and Langhoff get -1.38 a.u. at the MCPF level while Jaszuński *et al.* find its value to be -1.10 a.u. with CAS 6331, compared to our current basis 3 value of -1.27 a.u. and basis J

CCSD(T) value of -1.47 a.u. The other component, β_{zzz} , is -9.29 a.u. for MCPF, -8.85 for the CAS 6331, and -9.43 a.u. for basis J . Our current basis 3 CCSD(T) β_{zzz} of -9.62 a.u. has the largest magnitude. Selecting *all* these upper limit, correlated values for the components of β and γ , the largest latter components are our current basis 3 values shown in Table IX [for comparison the J basis values are $\gamma_{zzz} = 383$, $\gamma_{zzx} = 600$, $\gamma_{zzx} = 161$, $\gamma_{zzx} = 200$ (210 in basis 3)] together with the largest vibrational average and dispersion correction taken from the MCLR results, we obtain the final, estimated CCSD(T) result in Table XIX. This procedure would seem to offer an *upper bound* to the magnitudes of $\chi_{||}^{(2)}$ and $\chi_{||}^{(3)}$ that can be justified by *all* calculations. Obviously, such an estimate should not be considered to be superior to calculations that have included all effects consistently, as there are mutual interactions within a given basis and level of calculation that will result in a balance in the sizes of tensor components that should certainly be more appropriate in a rigorous calculation than taking the largest individual components. Similarly, our smaller correlated vibrational correction is not necessarily less accurate than the MCLR value as the absence of CI can be important; nor is the larger MCLR dispersion, though more justified, necessarily the most reliable. Nonetheless, we obtain final limit values of -3.9 and 57 for the electric susceptibilities. This estimated bound still shows about a 17%–19% error compared to the center of the experimental values. However, taking the lower limits from the error bars, we would have -3.9 compared to -4.3 and 57 compared to 60, which would fall within the 10% error we would expect. Obviously, however, this seems to be the *maximum* magnitude that can possibly be justified by any calculation to date. All "consistent" calculations give smaller magnitudes leaving unresolved the $\sim 20\%$ error for FH. In particular our best calculation gives -3.6 and 55 in the lone pair basis. Our best atom centered basis result is that in basis J , resulting in -3.6 and 50. Much larger basis calculations are reasonable and should be made; but in any event, we conclude that theory supports a value of $-3.6 \pm 0.3 \times 10^{-32}$ esu/molecule for $\chi_{||}^{(2)}$ and in $\chi_{||}^{(3)}$, $55 \pm 5 \times 10^{-39}$ esu/molecule. Finally, if we assume that CCSD(T) does not reliably measure the correct value of triples, and in particular, that the usually less reliable T(CCSD) is superior in this case, we would add -0.16 esu units to $\chi_{||}^{(2)}$ and 3 esu units to $\chi_{||}^{(3)}$, still within the specified error bars.

CONCLUSIONS

SCF theory predicts the magnitude of the hyperpolarizabilities to be smaller in comparison with SHG and dc-SHG experimental values for all molecules studied here typically by a factor of 2. Both the dispersion correction at the Hartree-Fock level (TDHF) and the correlation correction [MBPT(2), CCSD, or CCSD(T)] at the static level increase the magnitude. The theoretical values at the MBPT(2) correlated level augmented by the percentage dispersion correction evaluated by TDHF show good agreement with the dc-SHG experimental values for most

of the molecules. Overall agreement of the theoretical hyperpolarizabilities with experiment is encouraging for the application of this level of theory to larger systems. The polar molecules which have lone pairs and hydrogens are likely to be more difficult to describe well, as the basis set requirement seems to be more severe. At a minimum, at least one set of diffuse polarization basis functions must be added to the original polarizability consistent basis set for hydrogen, while additional functions must be added to the heavy atom basis. Because of H, vibrational effects are also likely to be more important for these molecules, and results should be corrected for that effect. By including the lone-pair functions, the comparatively high polarization of the lone-pair electrons can be described more properly. Alternatively, a large number of diffuse polarization functions including f , g , and $h \dots$ orbitals located on the heavy atom would be expected to perform the same task. The atom centered basis would offer more opportunity to extrapolate to the basis set limit than the lone pair basis procedure. The latter, however, has the effect of potentially eliminating any residual prejudice in standard basis generation methods. Consistencies between results in both types of bases recommends good (but not definitive) basis set convergence. At a given level of theory, all basis set improvements lead to larger $\gamma_{||}$ values.

Correlation effects are important for all the molecules studied. MBPT(2) tends to provide slightly larger values for both hyperpolarizabilities and fortuitously better agreement with experiment than does CCSD itself. However, the triple excitation effect as measured by CCSD(T) significantly improves upon the CCSD predictions for the β hyperpolarizability, with results usually moving somewhat closer to those obtained by MBPT(2). This suggests that MBPT(2) may offer an adequate measure of correlation for large molecule applications. Note, however, that for ethylene, the MBPT(2) estimate is too large. This may indicate that MBPT(2) might be insufficient for larger delocalized systems, such as linear polyenes.

Since any potential systematic error in a calculation is magnified when the experimental value is small, the small values for the hyperpolarizabilities of the FH molecule combined with the potential for a systematic error make it the most difficult case among the molecules studied. It seems that a discrepancy of about 20% between theory and experiment remains. Unless some unusual feature encountered in further investigation of basis sets, correlation, dispersion corrections, or other elements emerge, it seems unlikely that the remaining $\sim 20\%$ error—as small as it is—can be resolved. Experimentally, any population of excited vibrational states,^{32,33} in the experiment would dramatically increase $|\beta_{||}|$ and $|\gamma_{||}|$ and could account for the difference. Another experimental measurement would be welcome.

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